

THEORY OF TRANSLATIONAL ENERGY RELAXATION IN BINARY MIXTURES OF DILUTE GASES WITH CHEMICAL REACTION

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A simple approach to the process of translational energy relaxation in dilute gases due to Dahler, Malkin, Shizgal and others is extended to the case of systems with chemical reaction. Fundamental quantities characterizing the relaxation processes such as the relaxation time and collision numbers during this time are computed for a number of molecular models of the chemical reaction (the Prigogine-Xhrouet model, the line-of-centers model, a modified line-of-centers model, and reverse versions of these models). Results of this analytical theory are compared with the results of numerical simulations of solutions of the appropriate Boltzmann equation with the use of the modified Nanbu-Babovsky method. This comparison leads to very good agreement between the analytical theory and numerical calculations. A marked influence of the chemical reaction on the translational relaxation in a dilute gas is another important conclusion of this paper.

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1. Introduction

The problem of energy relaxation in many-component dilute gases is very important for the chemical kinetics, in systems with shock or detonation fronts and in many other situations. A simple intuitive theoretical description of the translational energy relaxation in two-component dilute mixtures of non-reactive gases was suggested by Malkin [1]. Such a description can be also obtained from the approach of Dahler and co-workers [2, 3]. A similar method was used for the analysis of relaxation of translational energy in perpendicular directions [4]. This method was verified by a numerical solution of the appropriate Boltzmann equation [5] and good agreement was obtained between analytical and numerical results. A similar comparison for the energy relaxation in a binary mixture of hard

spheres also produced good agreement between analytical theory and numerical computations [6].

An extension of the Boltzmann equation to a gaseous mixture of chemically reacting gases was suggested many years ago by Prigogine and co-workers [7, 8]. It is shown by these authors and also by many authors of subsequent investigations (see for example Ref. [9]) that a chemical reaction can perturb the velocity distribution functions of reacting gases and influence the rate of chemical reaction and also transport phenomena in such systems. Shizgal et al. developed a more advanced nonequilibrium theory of temperature relaxation in a binary gas [10, 11] and time dependent theory of hot atom reactions [12–14]. In Ref. [13] an expression for time derivative of one component's temperature resulting from elastic collisions between non-reactive gaseous components was derived from the Boltzmann equation and compared with the other expressions [15–17]. The expressions from Refs. [13] and [17] were shown to be equivalent. The other expressions [15, 16] have not a form of the relaxation equations in which a difference of temperatures usually appears. It should be emphasized that the expression from Ref. [6] is equivalent to the expressions of Shizgal [13] and Morse [17]. The time derivative of temperature for component of chemically reacting gas was calculated by Shizgal [18] using the Chapman–Enskog method of solution of the Boltzmann equation. The energy change during the process of electron attachment to molecules was considered by Shizgal et al. [19–21].

Generally speaking the temperature (mean kinetic energy) of reacting gas can change due to two effects (see Appendix for more explicit discussion of this point):

- (1) Energetic effect of this reaction.
- (2) Relaxation mechanism due to elastic collisions in the system.

In distinction to the effect (1) this relaxation mechanism is proportional to the energy difference between reacting components. In this paper we confine our attention exclusively to the point (2) neglecting the influence of energetic effects of chemical reaction on translational energy relaxation in the system (see Appendix). In distinction to this paper the authors of the papers quoted above [10–14, 18–21] considered a global influence of the chemical reaction on change of temperature of single reacting component. In consequence these authors did not analyze a simple description of temperature (or mean kinetic energy) relaxation in which the time derivative of energy is proportional to the difference of energies of reacting components.

We can expect that the effect of the chemical reaction on the relaxation phenomena in gases should be very significant because both the processes mentioned have the same tensor character (see Ref. [22]).

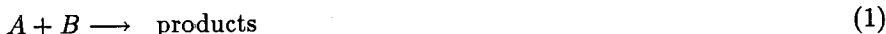
The aim of this paper is to extend the analytical description of translational energy relaxation in dilute gases suggested by Dahler and co-workers [2, 3] and by Malkin [1] to the important case of gaseous mixtures with chemical reaction and compare such an extension with results of the numerical solution of the appropriate Boltzmann equation. Following ideas of Malkin [1] we focus on the elastic collisions in the system with chemical reaction. In our approach the role of a chemical

reaction is confined to a modification of the elastic collision cross section. In this way we obtain generalizations of the well-known energy relaxation equation and expressions for the relaxation time accounting for simple models of chemical reaction in the system. To our knowledge such generalization has not been suggested so far in the literature. Using these expressions we derive analytical formulas for such quantities as the relaxation times and collision numbers during the relaxation time for various molecular models of chemical reactions. The results obtained from these analytical equations are compared with the computer results obtained by a direct simulation method of solution of the Boltzmann equation. Such Monte Carlo results play a role of missing experimental data. Preliminary results of the theory developed here was presented previously [23].

This paper is organized as follows. In Sec. 2 we specify the model of a dilute gas reacting chemically. Section 3 is devoted to the presentation of the theory of translational energy relaxation generalized to the case of a dilute binary gas with a chemical reaction and to the derivation of formulas characterizing the relaxation process and chemical reaction for specific molecular models. The scheme of numerical solution of the Boltzmann equation accounting for the chemical reaction is presented in Sec. 4. In Sec. 5 we analyze the comparison between the analytical and numerical results. The discussion of results obtained in this paper is presented in Sec. 6.

2. The model

We analyze a dilute gas composed of particles A and B in which the chemical reaction



takes place. We assume that the reaction (1) is in an initial state in which concentrations of products are negligibly small in comparison to concentrations of constituents A and B and that the collisions involving these products can be omitted in a description of the system. We assume also that the number densities of A and B fulfill the inequality:

$$n_A \ll n_B \quad (2)$$

and that the heat of reaction (1) $q_{\text{ch}} = 0$.

Following the idea of Prigogine and Xhrouet [7] we describe the elastic and inelastic intermolecular collisions using the concepts of the elastic differential cross section σ_{AB} and inelastic (reactive) collision probability α . In this paper we focus on two types of molecular models of the chemical reaction.

The first one can be associated with a common case of chemical reaction which can proceed when the relative kinetic energy of colliding molecules exceeds the threshold energy corresponding to a relative velocity g^* . To this category belong:

(a) The Prigogine-Xhrouet model [7]

$$[(1 - \alpha)\sigma_{AB}]^{\text{PX}} = \begin{cases} \frac{1}{4}d_{AB}^2, & g_{AB} \leq g^*, \\ 0, & g_{AB} > g^*, \end{cases} \quad (3)$$

where

$$d_{AB} = (d_A + d_B)/2, \quad (4)$$

d_A , d_B are diameters of molecules A and B modelled as hard spheres, g_{AB} is the relative velocity of colliding molecules. This model is in fact the simplest realization of a threshold relative velocity idea.

(b) The line-of-centers model of Present [24, 25]

$$[(1 - \alpha)\sigma_{AB}]^{LC} = \begin{cases} \frac{1}{4}d_{AB}^2, & g_{AB} \leq g^*, \\ \frac{1}{4}d_{AB}^2 g^{*2}/g_{AB}^2, & g_{AB} > g^*. \end{cases} \quad (5)$$

This model leads to the well-known Arrhenius type of expression for the temperature dependence of the rate of chemical reaction (see for example Ref. [26]).

(c) The same property has a modified version of the line-of-centers model which is in fact a simplified version of the simple reacting sphere model analyzed in detail by Xystris and Dahler [27]

$$[(1 - \alpha)\sigma_{AB}]^{mLC} = \begin{cases} \frac{1}{4}d_{AB}^2, & \mathbf{k} \cdot \mathbf{g}_{AB} \leq g^*, \\ 0, & \mathbf{k} \cdot \mathbf{g}_{AB} > g^*, \end{cases} \quad (6)$$

where \mathbf{k} is the unit vector parallel to the line joining the centers of colliding molecules.

The second type of chemical reactions considered in this paper is less common than the first one. It includes certain kinds of recombination and ion-molecular reactions in which low energy of relative motion of colliding molecules is necessary for reactive collisions. Such reactions can be sometimes characterized by a "negative" Arrhenius activation energy [28]. This type of chemical reaction can be associated with the following molecular models [28]:

(d) The reversed Prigogine-Xhrouet model

$$[(1 - \alpha)\sigma_{AB}]^{rPX} = \begin{cases} 0 & g_{AB} \leq g_L, \\ \frac{1}{4}d_{AB}^2, & g_{AB} > g_L. \end{cases} \quad (7)$$

(e) The reversed line-of-centers model

$$[(1 - \alpha)\sigma_{AB}]^{rLC} = \begin{cases} 0, & g_{AB} \leq g_L, \\ \frac{1}{4}d_{AB}^2 (1 - g_L^2/g_{AB}^2), & g_{AB} > g_L. \end{cases} \quad (8)$$

(f) The reversed modified line-of-centers model

$$[(1 - \alpha)\sigma_{AB}]^{rLC} = \begin{cases} 0, & \mathbf{k} \cdot \mathbf{g}_{AB} \leq g_L, \\ \frac{1}{4}d_{AB}^2, & \mathbf{k} \cdot \mathbf{g}_{AB} > g_L. \end{cases} \quad (9)$$

where g_L denotes the limiting value of the relative velocity of colliding molecules for the reactive collision.

3. Analytical theory

An essential idea put forward by Dahler and co-workers [2, 3] and presented in a very straightforward way by Malkin [1] can be summarized as follows. The

relaxation of translational energy in the two-component mixture of dilute gases can be described by the equation

$$\frac{d\langle E_A \rangle}{dt} = -\frac{1}{\tau} \langle E_A - E_B \rangle, \quad (10)$$

where E_A and E_B denote translational energies for components A and B , respectively, $\langle (\dots) \rangle$ denotes averaging over velocity distribution, τ denotes the relaxation time. Assuming that

$$E_B = 0, \quad (11)$$

we can write the following expression for the initial time ($t = 0$) of the equilibration process

$$\tau = -\frac{\langle (E_A)_0 \rangle}{(d\langle E_A \rangle/dt)_0}. \quad (12)$$

If we assume that the initial velocity distribution function of the component A can be described by the Maxwell-Boltzmann expression $f_A^{(0)}$, then

$$\langle (E_A)_0 \rangle = \int f_A^{(0)} \frac{m_A c_A^2}{2} d\mathbf{c}_A = \frac{3}{2} n_A k_B T_A, \quad (13)$$

where m_A , \mathbf{c}_A denote the mass and velocity of molecule A , whereas n_A and T_A are the number density and temperature of the component A , and k_B is the Boltzmann constant. Considering a gas without chemical reaction, analyzed by Dahler and co-workers [2, 3], Malkin [1] suggested the following simple expression:

$$\left(\frac{d\langle E_A \rangle}{dt} \right)_0 = \left\langle \frac{m_A}{2} \left[(c'_A)_0^2 - (c_A)_0^2 \right] \right\rangle_{\text{coll}} \quad (14)$$

where \mathbf{c}'_A is the velocity of molecule A after the elastic collision with molecule B (collisions between molecules A are neglected under the assumption expressed by Eq. (2)), $\langle (\dots) \rangle_{\text{coll}}$ denotes the following averaging within the collisional cylinder:

$$\langle (\dots) \rangle_{\text{coll}} = \int \int \int f_A^{(0)} f_B^{(0)} (\dots) \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B, \quad (15)$$

where $f_B^{(0)}$ denotes the Maxwell-Boltzmann velocity distribution function of particles B and Ω_{AB} is the solid angle. Let us observe that the velocity \mathbf{c}'_A can be expressed by relation [30]

$$\mathbf{c}'_A = \mathbf{c}_A + \frac{2m_B}{m_A + m_B} \mathbf{k} [\mathbf{k} \cdot (\mathbf{c}_B - \mathbf{c}_A)]. \quad (16)$$

On the other hand according to the assumption (11) we have

$$(\mathbf{c}_B)_0 = 0. \quad (17)$$

Substituting Eqs. (13) and (14) into Eq. (12) we obtain for hard spheres

$$\tau^{\text{HS}} = -\frac{3}{4} \frac{n_A k_B T_A}{m_A} \left\{ \left\langle \left[(c'_A)_0^2 - (c_A)_0^2 \right] \right\rangle_{\text{coll}} \right\}^{-1}. \quad (18)$$

Equation (18) can be generalized for the system with the chemical reaction (1) under conditions (2) and (11) in a spirit of the approach given by Prigogine and co-workers [7, 8]

$$\tau = -\frac{3}{4} \frac{n_A k_B T_A}{m_A} \left\{ \left\langle \left[(c'_A)_0^2 - (c_A)_0^2 \right] \right\rangle_{\text{coll}}^{\text{ch}} \right\}^{-1}, \quad (19)$$

where

$$\langle(\dots)\rangle_{\text{coll}}^{\text{ch}} = \int \int \int f_A^{(0)} f_B^{(0)} (\dots) (1 - \alpha) \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B. \quad (20)$$

Equation (19) is the starting point of our analytical theory. The difference between this equation and the approaches used in the literature is discussed in Appendix. Before performing detailed calculations for chosen molecular models of chemical reaction let us introduce some useful quantities. We define the collision frequency of elastic collisions as

$$N_{AB}^{\text{el}} = \langle(1)\rangle_{\text{coll}}^{\text{ch}}. \quad (21)$$

In the absence of the chemical reaction (1) N_{AB}^{el} coincides with the total collision frequency N_{AB}^{HS} for the gas composed of hard spheres. If the chemical reaction (1) takes place the reactive collision frequency can be defined by the relation

$$N_{AB}^{\text{re}} = N_{AB}^{\text{HS}} - N_{AB}^{\text{el}}. \quad (22)$$

We can also introduce the collision numbers during the relaxation time

$$Z = \tau(N_{AB}^{\text{HS}})_0/n_A, \quad (23)$$

$$Z_{\text{el}} = \tau(N_{AB}^{\text{el}})_0/n_A, \quad (24)$$

$$Z_{\text{re}} = \tau(N_{AB}^{\text{re}})_0/n_A, \quad (25)$$

where the subscripts "0" are used to indicate that the calculations are performed at $t = 0$. On the other hand N_{AB}^{re} can be related to the rate of the chemical reaction (1)

$$(N_{AB}^{\text{re}})_0 = -\frac{dn_A}{dt} = kn_A n_B, \quad (26)$$

where k is the rate constant. Taking into account Eq. (2) we get

$$n_A = (n_A)_0 \exp(-kn_B t) = (n_A)_0 \exp(-t/\tau_{\text{ch}}), \quad (27)$$

where the relaxation time for chemical reaction (1) reads

$$\tau_{\text{ch}} = 1/kn_B. \quad (28)$$

Comparing Eqs. (25), (26), and (28) we get the relation

$$Z_{\text{re}} = \tau/\tau_{\text{ch}}. \quad (29)$$

Before calculating the quantities τ , N_{AB}^{el} , N_{AB}^{re} , Z , Z_{el} , and Z_{re} introduced above, let us briefly discuss how the problems considered in this paper are related to the central problem of the chemical kinetics, i.e. the calculation of the rate of chemical reaction.

In this paper we analyze rather the special situation when two reacting components have different temperatures T_A and T_B . Such a situation can be realized in systems with chemical reactions (see e.g. Refs. [14, 31-33]). In this situation the rate of chemical reaction is defined by the relation

$$\begin{aligned} v_{\text{ch}}(T_A, T_B) &= -\frac{dn_A}{dt} = \\ &= \int \int \int f_A(T_A) f_B(T_B) \alpha \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B. \end{aligned} \quad (30)$$

Assuming that the chemical reaction does not perturb significantly the molecular velocity distribution, we can replace functions $f_A(T_A)$ and $f_B(T_B)$ by the Maxwell-Boltzmann distributions for temperatures T_A and T_B . Substituting these distributions into Eq. (30) and changing variables c_A and c_B to new variables G_T and g_{AB} defined by the relations

$$G_T = \frac{m_A/T_A}{m_A/T_A + M_B/T_B} c_A + \frac{m_B/T_B}{m_A/T_A + M_B/T_B} c_B \quad (31)$$

$$g_{AB} = c_A - c_B \quad (32)$$

and using the well-known line-of-centers model (Eq. (5)), we get the following expression for the rate of chemical reaction:

$$v_{ch}(T_A, T_B) = 2n_A n_B d_{AB}^2 [2\pi k_B (T_A/m_A + T_B/m_B)]^{1/2} \times \exp \left[-\frac{g^{*2}}{2k_B (T_A/m_A + T_B/m_B)} \right] \quad (33)$$

Equation (33) is a generalization of the well-known rate expression for the collisional theory of chemical kinetics [26] to the case of the two-temperature system and can be reduced to this expression by substitution $T_A = T_B$. An equivalent expression was obtained by Shizgal and Fitzpatrick [12].

Relating Eq. (33) to the model considered in this paper we can notice that the condition (11) can be written as

$$T_B = 0. \quad (34)$$

Substituting Eq. (34) to Eq. (33) we get

$$N_{AB}^{re} = v_{ch}(T_B = 0) = 2n_A n_B d_{AB}^2 (2\pi k_B T_A/m_A)^{1/2} \exp(-\varepsilon^*), \quad (35)$$

where

$$\varepsilon^* = E^* m_A / m_{AB} k_B T_A, \quad (36)$$

$$E^* = m_{AB} g^{*2} / 2, \quad (37)$$

$$1/m_{AB} = 1/m_A + 1/m_B. \quad (38)$$

Now we proceed to the calculation of explicit expressions of the quantities N_{AB}^{el} , τ , Z , Z_{el} , Z_{re} characterizing the translational energy relaxation in the system considered. Similarly to Eq. (36) we define

$$\varepsilon_L = E_L m_A / m_{AB} k_B T_A, \quad (39)$$

where

$$E_L = m_{AB} g_L^2 / 2. \quad (40)$$

Substituting definitions (3)–(9) into Eqs. (20) and (21) we get

$$N_{AB}^{el} = 2n_A n_B d_{AB}^2 (2\pi k_B T_A/m_A)^{1/2} M_N^i, \quad (41)$$

where for $i = \text{HS, PX, LC, mLC, rPX, rLC, rmLC}$ corresponding to the system of hard spheres without the chemical reaction, the model of Prigogine-Xhrouet (Eq.(3)), the line-of-centers model (Eq. (5)), the modified line-of-centers model (Eq. (6)), the reverse Prigogine-Xhrouet model (Eq. (7)), the reverse line-of-centers

model (Eq. (8)) and the reverse modified line-of-centers model (Eq. (9)), respectively, we obtain the following expressions:

$$M_N^{\text{HS}} = 1, \quad (42)$$

$$M_N^{\text{PX}} = 1 - (\varepsilon^* + 1) \exp(-\varepsilon^*), \quad (43)$$

$$M_N^{\text{LC}} = M_N^{\text{mLC}} = 1 - \exp(-\varepsilon^*), \quad (44)$$

$$M_N^{\text{rPX}} = (\varepsilon_L + 1) \exp(-\varepsilon_L), \quad (45)$$

$$M_N^{\text{rLC}} = M_N^{\text{rmLC}} = \exp(-\varepsilon_L). \quad (46)$$

Let us notice that expressions for N_{AB}^{re} can be obtained from expressions for N_{AB}^{el} taking into account Eq. (22). Substituting Eqs. (3)–(9) into Eq. (19) we get

$$\tau = \frac{3}{16} \frac{(m_A + m_B)^2}{m_A m_B} \left(\frac{m_A}{2\pi k_B T_A} \right)^{1/2} \frac{1}{d_{AB}^2 n_B} M_\tau^i, \quad (47)$$

where for $i = \text{HS, PX, LC, mLC, rPX, rLC, rmLC}$ which have an analogous meaning as described above, we obtain

$$M_\tau^{\text{HS}} = 1, \quad (48)$$

$$M_\tau^{\text{PX}} = \left[1 - \frac{1}{2} (\varepsilon^{*2} + 2\varepsilon^* + 2) \exp(-\varepsilon^*) \right]^{-1}, \quad (49)$$

$$M_\tau^{\text{LC}} = \left[1 - \frac{1}{2} (\varepsilon^* + 2) \exp(-\varepsilon^*) \right]^{-1}, \quad (50)$$

$$M_\tau^{\text{mLC}} = [1 - (\varepsilon^* + 1) \exp(-\varepsilon^*)]^{-1}, \quad (51)$$

$$M_\tau^{\text{rPX}} = \left[\frac{1}{2} (\varepsilon_L^2 + 2\varepsilon_L + 2) \exp(-\varepsilon_L) \right]^{-1}, \quad (52)$$

$$M_\tau^{\text{rLC}} = \left[\frac{1}{2} (\varepsilon_L + 2) \exp(-\varepsilon_L) \right]^{-1}, \quad (53)$$

$$M_\tau^{\text{rmLC}} = [(\varepsilon_L + 1) \exp(-\varepsilon_L)]^{-1}. \quad (54)$$

In an analogous way we obtain from Eq. (23)

$$Z = \frac{3}{8} \frac{(m_A + m_B)^2}{m_A m_B} M_Z^i, \quad (i = \text{HS, PX, LC, mLC, rPX, rLC, rmLC}) \quad (55)$$

$$M_Z^i = M_\tau^i \quad (56)$$

and also from Eqs. (24) and (25)

$$Z_{\text{el}} = \frac{3}{8} \frac{(m_A + m_B)^2}{m_A m_B} M_{Z_{\text{el}}}^i, \quad (i = \text{HS, PX, LC, mLC, rPX, rLC, rmLC}) \quad (57)$$

where

$$M_{Z_{\text{el}}}^{\text{HS}} = 1, \quad (58)$$

$$M_{Z_{\text{el}}}^{\text{PX}} = \frac{1 - (\varepsilon^* + 1) \exp(-\varepsilon^*)}{1 - \frac{1}{2} (\varepsilon^{*2} + 2\varepsilon^* + 2) \exp(-\varepsilon^*)}, \quad (59)$$

$$M_{Z_{cl}}^{LC} = \frac{1 - \exp(-\varepsilon^*)}{1 - \frac{1}{2}(\varepsilon^* + 2)\exp(-\varepsilon^*)}, \quad (60)$$

$$M_{Z_{cl}}^{mLC} = \frac{1 - \exp(-\varepsilon^*)}{1 - (\varepsilon^* + 1)\exp(-\varepsilon^*)}, \quad (61)$$

$$M_{Z_{cl}}^{rPX} = 2 / \left[\varepsilon_L + 1 + (\varepsilon_L + 1)^{-1} \right], \quad (62)$$

$$M_{Z_{cl}}^{iLC} = 2 / (\varepsilon_L + 2), \quad (63)$$

$$M_{Z_{cl}}^{rmLC} = 1 / (\varepsilon_L + 1) \quad (64)$$

and

$$Z_{re} = \frac{3(m_A + m_B)^2}{8 m_A m_B} M_{Z_{re}}^i, \quad (65)$$

where

$$M_{Z_{re}}^{HS} = 0, \quad (66)$$

$$M_{Z_{re}}^{rPX} = \frac{(\varepsilon^* + 1)\exp(-\varepsilon^*)}{1 - \frac{1}{2}(\varepsilon^{*2} + 2\varepsilon^* + 2)\exp(-\varepsilon^*)}, \quad (67)$$

$$M_{Z_{re}}^{LC} = \frac{\exp(-\varepsilon^*)}{1 - \frac{1}{2}(\varepsilon^* + 2)\exp(-\varepsilon^*)}, \quad (68)$$

$$M_{Z_{re}}^{mLC} = \frac{\exp(-\varepsilon^*)}{1 - (\varepsilon^* + 1)\exp(-\varepsilon^*)}, \quad (69)$$

$$M_{Z_{re}}^{rPX} = \frac{2(\exp \varepsilon_L - \varepsilon_L - 1)}{\varepsilon_L^2 + 2\varepsilon_L + 2}, \quad (70)$$

$$M_{Z_{re}}^{iLC} = \frac{2(\exp \varepsilon_L - 1)}{\varepsilon_L + 2}, \quad (71)$$

$$M_{Z_{re}}^{rmLC} = \frac{\exp \varepsilon_L - 1}{\varepsilon_L + 1}. \quad (72)$$

These results for Z_{re} are especially interesting because of Eq. (29).

4. Numerical simulations

In order to compare the analytical results presented in Sec. 3 with the results obtained by numerical solution of the Boltzmann equation we apply the so-called direct simulation scheme. Starting in 1960's with Bird [34, 35] several algorithms were introduced [36, 37] in 1970's. In 1980 Nanbu proposed a scheme that could be based on the Boltzmann equation in a very satisfying manner [38, 39]. An overview of the methods mentioned is given in Ref. [40]. Bird's scheme is the most effective and most frequently used, although some doubts arose concerning artefacts (see Ref. [36] et loc. cit.). Babovsky [41] introduced a modification of Nanbu's method which made its efficiency comparable to that of the Bird method [42-44]. In order to deal with chemical reactions and relaxation of energy we introduce small changes (possible only for small time increments). This method has been already used successfully in the previous papers [5, 6].

We now recapitulate the main ideas of this scheme. We take into account that the probability P_{ij} of collision between two spheres i and j is

$$P_{ij} = (\Delta V)_{ij}/V, \quad (73)$$

where V is the volume of the system analyzed and $(\Delta V)_{ij}$ is the volume of the collision cylinder for the spheres i and j

$$(\Delta V)_{ij} = \pi d^2 g_{ij} \Delta t, \quad (74)$$

where Δt is a time step and $d = d_A = d_B$ because we assume that the colliding spheres have identical diameters. Equations (73) and (74) are used in our simulations for which we perform R runs in order to diminish fluctuations connected with a small number of particles I in the system considered.

Let us now briefly characterize the simulation scheme.

A typical run is carried out in the following way:

I. During the first time step $\Delta t = t_0$ we perform the following operations:

(a) We put i equal to one.

(b) For the particle i only one partner is randomly chosen from the $I - 1$ remaining particles. An (elastic or reactive) collision between the particles i and j is carried out with the probability $(I - 1)P_{ij}/2$. If no collisions occur the velocities remain unchanged. Otherwise we decide, according to the model applied (e.g. the line-of-centers model), if the collision is an elastic or a reactive one. In the case of an elastic collision both of the velocities (different from Nanbu's simulation scheme [38–40], because t_0 is small enough) are changed according to the collision equations of hard spheres. We introduce as in Refs. [38–43] a randomly chosen g_{ij} . If the collision is a reactive one the molecular velocities remain unchanged, for we neglect its influence on the velocity distribution.

(c) The procedure (b) is repeated for the next i and so on up to i being equal to I .

II. Now (a), (b), and (c) are performed for the second time step and so on. After each time step the kinetic energies and numbers of reactive and elastic collisions are collected for the final evaluation.

Then another initial situation can be created for the next run. R runs are carried out. Each result presented in this paper is an arithmetic mean over all R runs. We get values for energies, temperatures of the components A and B as well as an average of the numbers of elastic and reactive collisions.

We chose the following system for numerical simulations. A volume $V = 1666.7 \text{ nm}^3$ contain 50 spheres A and 450 spheres B having diameters $d_A = d_B = 0.35 \text{ nm}$ and masses $m_A = m_B = 16 \text{ g/mole}$. This corresponds to the packing fraction of 0.0067348. At the beginning of the relaxation process distributions of molecular velocities c_A and c_B corresponded to the temperatures of $T_A = 600 \text{ K}$ and $T_B = 0 \text{ K}$, respectively. We performed 1000 runs R for 5 time steps $\Delta t = t_0 = 0.6941 \times 10^{-13} \text{ s}$. Because $t_0 \ll \tau$ we assume that the time interval $5t_0$ is short enough for the equilibration process to be in its initial state and that it is sufficient to obtain the results for the relaxation time τ using a simple formula which follows from Eq. (12)

$$\tau = -5\Delta t E_A^{(0)} / (E_A^{(5)} - E_A^{(0)}), \quad (75)$$

where superscripts (0) and (5) are used to denote the values of E_A after 0 and 5 time steps, respectively.

5. Results of analytical theory and numerical simulations

In order to compare results of the analytical theory presented in Sec. 3 and results of numerical simulations described in Sec. 4, in Figs. 1-7 we plotted quantities describing the translational energy relaxation for the system characterized by various molecular models (Eqs. (3)-(9)) of the chemical reaction (1). The dependence of these quantities on reduced energies ϵ^* and ϵ_L obtained from various

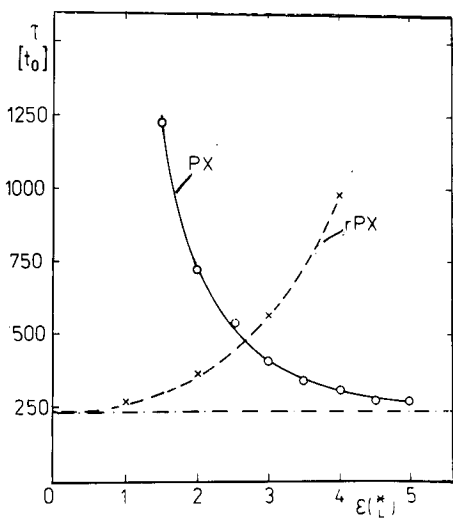


Fig. 1

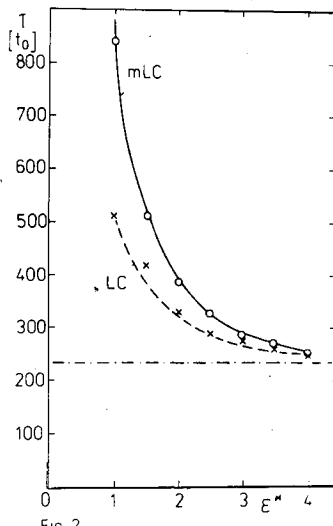


Fig. 2

Fig. 1. The relaxation time τ (in time step units t_0) as a function of appropriate reduced energy $\epsilon \left(\frac{*}{L} \right)$, i.e. ϵ^* and ϵ_L for the PX and rPX models, respectively (see Eqs. (3) and (7)). For the PX model the analytical results obtained from Eqs. (47) and (49) for $m_A = m_B$ are represented by the solid line and the computer simulation results by the small circles. For the rPX model the dashed line is obtained from Eqs. (47) and (52) and the computer results are represented by small crosses. The dotted line shows the asymptotic value of τ for $\epsilon^* \Rightarrow \infty$ and $\epsilon_L \Rightarrow 0$ for the PX and rPX models, respectively.

Fig. 2. The relaxation time τ (in time step units t_0) as a function of the reduced threshold energy ϵ^* . For the LC and mLC models (see Eqs. (5) and (6)) the analytical results (see Eqs. (47), (50) and (51)) for $m_A = m_B$ are represented by the dashed and solid lines and compared with the computer simulation results represented by small crosses and circles, respectively. The dotted line represents the asymptotic value of τ for $\epsilon^* \Rightarrow \infty$, i.e. in the absence of chemical reaction.

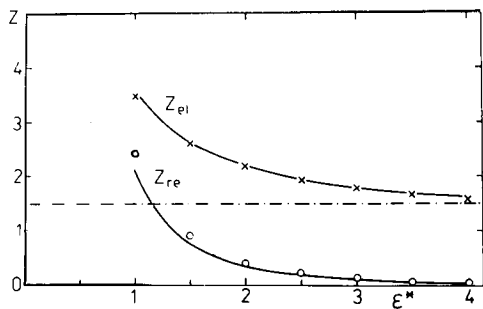


Fig. 3

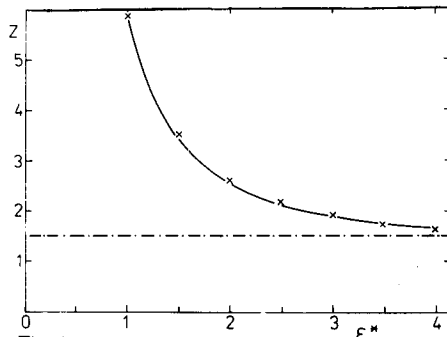


Fig. 4

Fig. 3. The elastic and reactive collision numbers Z_{el} and Z_{re} (see Eqs. (24) and (25)) for the mLC model (see Eq. (6)) for $m_A = m_B$ as a function of the reduced threshold energy ε^* . The computer simulation results for Z_{el} and Z_{re} are represented by the small crosses and circles, respectively. The analytical results (see Eqs. (57), (61), (65), and (69)) are represented by the solid lines. The dotted line shows the asymptotic value of Z_{el} for $\varepsilon \Rightarrow \infty$.

Fig. 4. The total collision number Z (see Eq. (23)) for the mLC model (see Eq. (6)) for $m_A = m_B$ as a function of the reduced threshold energy ε^* . The analytical (see Eqs. (55), (56), and (51)) and computer simulation results are represented in a similar way as in Fig. 3.

analytical expressions derived in Sec. 3 (Eqs.(41)–(72)) is represented by continuous (solid or dashed) lines. Results of numerical simulations of the solutions of the appropriate Boltzmann equation are represented by points (small circles or crosses).

Generally we can notice very good agreement between two types of the above-mentioned results (see Figs. 1–4). Another obvious observation is a very strong dependence of the quantities characterizing the translational energy relaxation (e.g. the relaxation time τ defined by Eq. (19)) on the chemical reaction in the system. This dependence is characterized by a significant upward deviation of these quantities from the values for systems without chemical reaction ($\varepsilon^* \Rightarrow \infty$, $\varepsilon_L \Rightarrow 0$) with diminishing ε^* or growing ε_L .

It is interesting to observe that for the line-of-centers model (see Eq. (5)) Shizgal [18] analyzed the influence of nonequilibrium effects on the rate of time derivative of temperature of reacting component. This author shows that for ε^* diminishing from 2 to 1, i.e. in the region in which the largest effects of the chemical reaction on the energy relaxation obtained from the Maxwellian velocity distribution function (see Figs. 2–4), the role of nonequilibrium effects is relatively small. However, a direct comparison of our results with those from Ref. [18] is impossible because of the differences discussed in Appendix.

Let us observe that we include the effect of chemical reaction on the translational energy relaxation in an implicit way only, i.e. by excluding the collisions

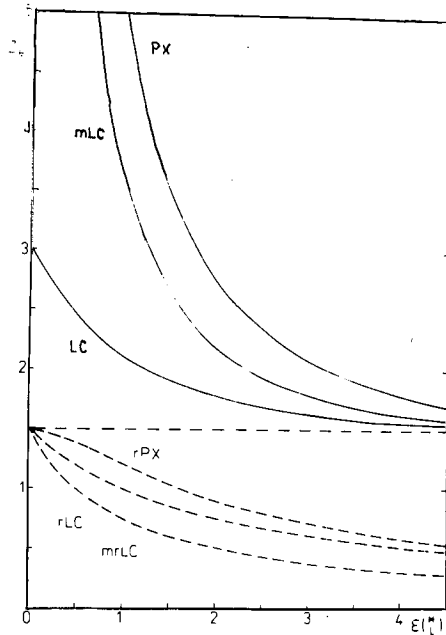


Fig. 5. The elastic collision number Z_{el} (see Eq. (24)) for $m_A = m_B$ as a function of the appropriate reduced energy $\epsilon \left(\frac{*}{L} \right)$ (see Fig. 1). The analytical results for the PX, LC, and mLC models (see Eqs. (3), (5), and (6)) are calculated from Eqs. (57) and (59)–(61) and represented by the solid lines and those for the rPX, rLC, and rmLC models (see Eqs. (7)–(9)) are calculated from Eqs. (57), and (62)–(64) and represented by the dashed lines. The dotted line shows the limiting hard sphere value for Z_{el} .

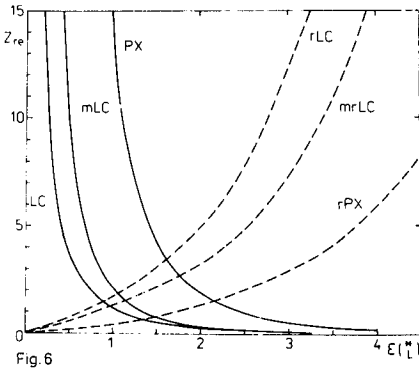


Fig. 6. The reactive collision number Z_{re} (see Eq. (25)) for the models analyzed represented in the same way as in Fig. 5. (see Eqs. (65)–(72) with $m_A = m_B$).

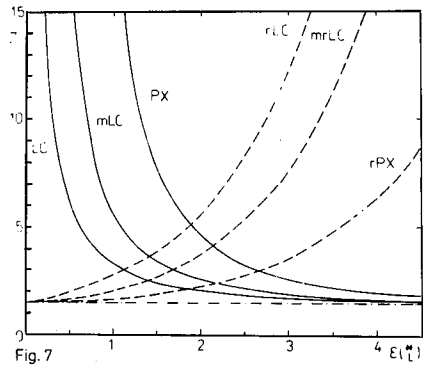


Fig. 7. The total collision number Z (see Eq. (23)) for the models analyzed represented in the same way as in Fig. 5 (see Eqs. (55), (56) and (48)–(54)).

with parameters leading, according to the molecular models (Eqs. (3)–(9)), to the chemical reaction.

We would like to emphasize that the neglecting of the influence of the chemical reaction on the velocity distribution during a time of the order of τ seems to be somewhat artificial if τ_{ch} is not large enough in comparison to τ . In other cases (i.e. for small ε^* and large ε_L) our model realized in calculations and in simulations seems to be realistic for the beginning of the translational energy equilibration. In a more general treatment a disappearance of particles A after reactive collisions should be taken into account.

Neglecting of products and changes in the velocity distribution of particles B seems to be a good approximation in all cases in which the concentration of particles A is sufficiently small.

The influence of the chemical reaction on the velocity distribution and a possible change of the relaxation time connected with this effect should be examined in another model system. We hope to do such simulations for the fast reactions in future. However, this problem must be treated with another simulation scheme in which the heat bath particles do not occur explicitly in order to be able to deal with large particle numbers of the sort A . Otherwise the statistics would become too poor when a great part of the particles A disappears.

It is also interesting to discuss in some details comparison between results for the line-of-centers model and the modified line-of-centers model. The original line-of-centers model expressed by Eq. (5) was used by many authors for calculation of nonequilibrium corrections to the rate of chemical reactions in dilute gases (see e.g. Refs. [9] and [45] and publications cited therein). However, we believe that the essential physical idea of this model is expressed in a more fundamental way by Eq. (6) which we call the modified line-of-centers model. In fact both the models expressed by Eqs. (5) and (6) lead to the same formula for the rate of chemical reaction (1) in dilute gases. This does not necessarily mean that both above-mentioned models are equivalent. For example, both analytical and numerical results for the translational energy relaxation time for the LC and mLC models displayed in Fig. 2 produced a markedly different behavior for these models. The difference between these models is the most pronounced for the elastic collision number Z_{el} which, as it can be seen from Fig. 5, increases to infinity with $\varepsilon^* \Rightarrow 0$ for the mLC model only.

6. Discussion

A description of the problem of relaxation of translational energy in dilute chemically non-reactive gases was suggested by Dahler and co-workers [2, 3] and by Malkin [1]. It can be observed that the equivalent results were obtained also by Shizgal [13]. We suggest in this paper how to generalize this approach to the case of dilute gas with chemical reaction using an idea analogous to the generalization of the Boltzmann equation suggested by Prigogine and co-workers [7, 8] for systems with chemical reactions. Expressions for the relaxation time (see Eq. (19)) and the collision numbers (see Eqs. (23)–(25)) were obtained in this way for various molecular models of chemical reactions (see Eqs. (3)–(9)). In order to verify this

idea we have calculated these quantities from analytical expressions characterizing the energy relaxation in a dilute gas (see Eqs. (47) and (55), (57) and (65)) and compared them with the results obtained from the modified Nambu-Babovsky method [5, 6] of numerical simulations of the solution of the appropriate Boltzmann equation. Comparison of the analytical theory (Eqs. (41)–(72)) and results of numerical simulations lead to the following conclusions:

(a) There is very good agreement between the analytical theory and numerical simulations for all models of chemical reaction considered in this paper (see Eqs. (3)–(9)). This conclusion strongly supports our conviction that Eq. (19) is a reasonable extension of the description of translational energy relaxation process due to Dahler and others [2, 3] and Malkin [1] to the case of a dilute gas with chemical reaction (1). We think that the analytical expressions for translational energy relaxation time (see Eq. (47)), as well as for the total (see Eq. (55)), elastic (see Eq. (57)) and reactive (see Eq. (65)) collision numbers obtained from Eq. (19) with the use of appropriate reactive collision probabilities maybe used to understand better the behavior of these quantities in real systems with chemical reactions.

(b) Application of the modified line-of-centers model mLC (see Eq. (6)) for analysis of the energy relaxation process leads to qualitatively different results (see Fig. 5) than those obtained with the line-of-centers model LC (see Eq. (5)).

(c) The chemical reaction (1) can very strongly influence the translational energy relaxation, especially in cases of small ε^* or large ε_L which corresponds to the situation when a large portion of scattering events in the system leads to the chemical reaction. This conclusion is easy to be understood from the point of view of irreversible thermodynamics. A detailed discussion of chemical reaction and relaxation phenomena presented, for example, by De Groot and Mazur [22] indicates that these processes have a very similar nature and strong interaction between them can be expected.

Appendix

The basic equation of our theory (Eq. (19)) was introduced in Sec. 3 in an intuitive way. It would be instructive to derive this equation from the Boltzmann equation. The Boltzmann equation according to Eq. (1) and inequality (2) can be written in the form introduced by Prigogine and Xhrouet [7]

$$\begin{aligned} \frac{\partial f_A}{\partial t} = & \int \int (f'_A f_B^{(0)'} - f_A f_B^{(0)}) (1 - \alpha) \sigma_{AB} g_{AB} d\Omega_{AB} dc_B \\ & - \int \int f_A f_B^{(0)} \alpha \sigma_{AB} g_{AB} d\Omega_{AB} dc_B, \end{aligned} \quad (\text{A1})$$

where f'_A and $f_B^{(0)'}$ denote the velocity distribution functions after collision. Multiplying both sides of Eq. (A1) by $m_A c_A^2/2$, integrating over c_A and taking into account that

$$dc_A dc_B = dc'_A dc'_B, \quad (\text{A2})$$

we obtain

$$\begin{aligned} \frac{d\langle E_A \rangle}{dt} = & \int \int \int f_A f_B^{(0)} \frac{m_A}{2} [(c'_A)^2 - c_A^2] (1 - \alpha) \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B \\ & - \int \int \int f_A f_B^{(0)} \frac{m_A c_A^2}{2} \alpha \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B. \end{aligned} \quad (\text{A3})$$

The first term on the right hand side of Eq. (A3) denotes the process of equilibration of energies due to elastic collisions in the system. The second term on this side of Eq. (A3) is connected with the energetic effect of the chemical reaction (1) and can be also written in the form [7]

$$- \int \int \int f_A f_B^{(0)} \frac{m_A c_A^2}{2} \alpha \sigma_{AB} g_{AB} d\Omega_{AB} d\mathbf{c}_A d\mathbf{c}_B = v_{\text{ch}} \Delta \varepsilon, \quad (\text{A4})$$

where $\Delta \varepsilon$ is the energetic effect of chemical reaction. We have taken into account that due to inequality (2)

$$(\partial f_B / \partial t)_{\text{ch}} = 0, \quad (\text{A5})$$

where $(\partial f_B / \partial t)_{\text{ch}}$ denotes the change of the distribution function of the component B due to the chemical reaction (1). If we neglect the energetic effect of the reaction (1) and put

$$\Delta \varepsilon = 0 \quad (\text{A6})$$

and approximate f_A in Eq. (A3) by the Maxwell-Boltzmann distribution

$$f_A \cong f_A^{(0)}, \quad (\text{A7})$$

we can obtain Eq. (19) using Eqs. (12) and (13). Thus, we see that our intuitive result in the form of Eq. (19) can be obtained directly from the Boltzmann equation if we focus on the relaxation mechanism due to the elastic collisions in the system and neglect the energetic effects of the chemical reaction and deviations from the Maxwell-Boltzmann distribution due to this reaction. Doing this we obtain a simple description of the energy relaxation in the system with chemical reaction in the traditional form similar to Eq. (14) which allows easily to define the relaxation time τ . Comparison of this theory with numerical solution of the Boltzmann equation with the Nanbu-Babovsky method leads to the conclusion that our approach can be fairly accurate in many situations. It should be pointed out that calculations of the energy (or temperature) relaxation in systems with chemical reactions presented in many papers by Shizgal and co-workers [12-14, 18, 20, 21] were based, in contrast to our approach, on Eq. (A3) with the second term on the right hand side included. In consequence these authors did not consider the relaxation process defined by Eq. (10) and the following Eqs. (12), (13), and (19).

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